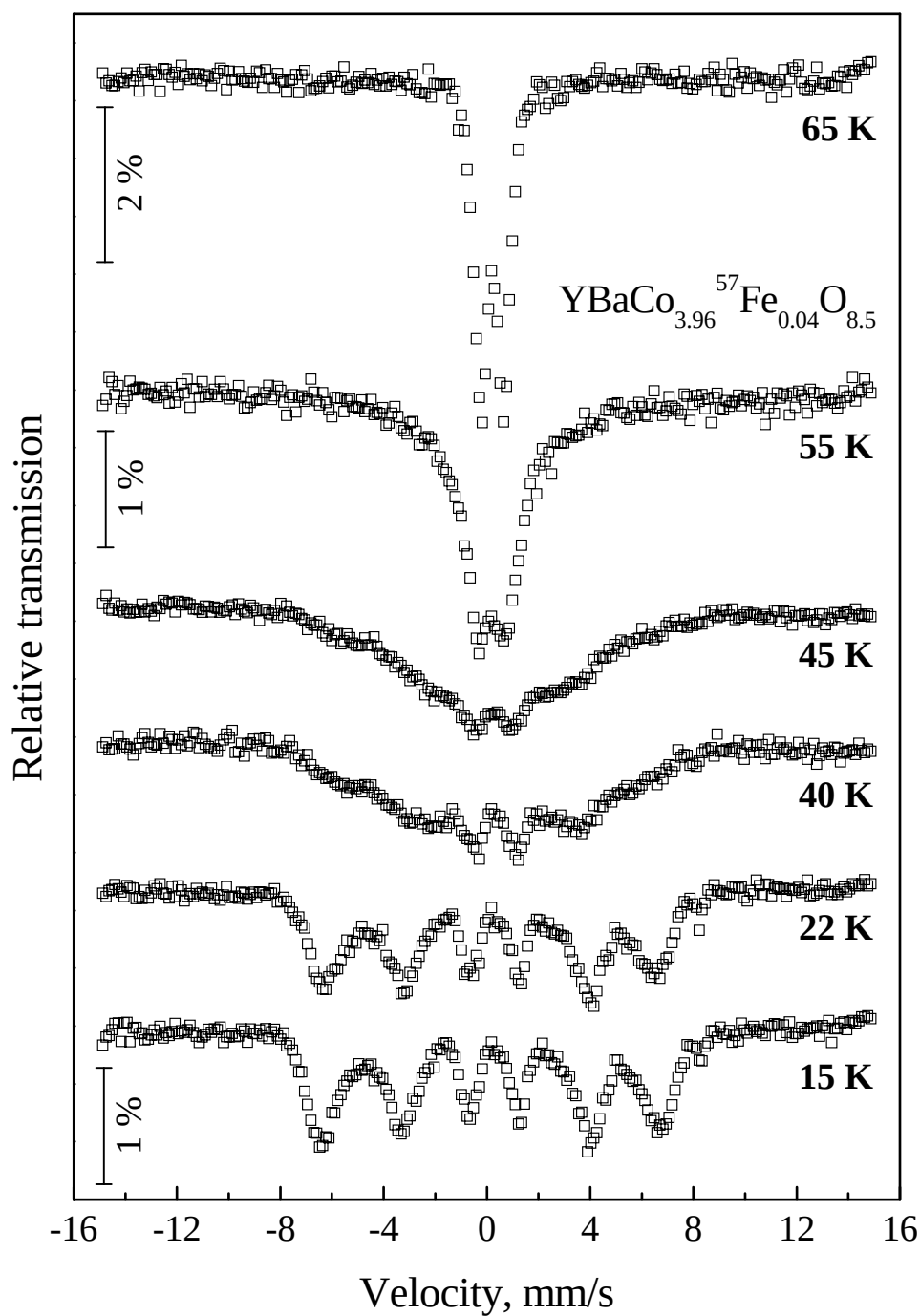


Electronic Supplementary Information:



Selected Mössbauer spectra of $\text{YBaCo}_{3.96}^{57}\text{Fe}_{0.04}\text{O}_{8.5}$ in the vicinity of T_{MF} .

Typical distribution of the cobalt-oxygen polyhedra fractions in consecutive layers parallel to the *a-b* plane of simulated YBaCo₄O_{8.5}, extracted from the MD results at 150 K*

Layer designation	Polyhedron fraction in the layer		
	N _{crd} = 4	N _{crd} = 5	N _{crd} = 6
<i>Co2</i>	0.054	0.717	0.229
<i>Co1</i>	0.075	0.712	0.213
<i>Co2</i>	0.042	0.658	0.300
<i>Co1</i>	0.050	0.887	0.063
<i>Co2</i>	0.042	0.775	0.183
<i>Co1</i>	0.025	0.838	0.137
<i>Co2</i>	0.021	0.733	0.246
<i>Co1</i>	0.038	0.887	0.075
<i>Co2</i>	0.033	0.725	0.242
<i>Co1</i>	0.037	0.850	0.113
<i>Co2</i>	0.021	0.746	0.233
<i>Co1</i>	0.062	0.825	0.113
<i>Co2</i>	0.033	0.696	0.271
<i>Co1</i>	0.037	0.838	0.125
<i>Co2</i>	0.029	0.717	0.254
<i>Co1</i>	0.025	0.862	0.113
<i>Co2</i>	0.046	0.717	0.237
<i>Co1</i>	0.037	0.825	0.138
<i>Co2</i>	0.029	0.696	0.275
<i>Co1</i>	0.062	0.850	0.088

* Cut-off distance of the Co-O bonds is 2.5 Å.
** *Co1* and *Co2* correspond to the triangular and Kagomé-type layers in YBaCo₄O₇ structure, respectively.